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Appendix E

**Title: Patterning Electroluminescent Materials with Feature
Sizes as Small as 5 μm Using Elastomeric Membranes as Masks for Dry Lift-Off**

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Patterning Electroluminescent Materials with Feature Sizes as Small as 5 μm Using Elastomeric Membranes as Masks for Dry Lift-Off**

By David C. Duffy, Rebecca J. Jackman, Kathleen M. Vaeth, Klavs F. Jensen*, and George M. Whitesides*

This communication describes the use of elastomeric membranes as conformal masks to pattern electroluminescent (EL) materials at feature sizes ranging from 5 μm to 500 μm . There is currently great interest in EL organic materials primarily because of their potential use in optical devices, especially flat panel displays.^[1–4] Simple and reliable methods to pattern arrays of small (< 100 μm) features of these materials, which could function as pixels when addressed individually, are needed in order for them to be used in high resolution displays. Several methods have been used to pattern EL materials previously: photolithography followed by lift-off,^[5–7] rigid shadow masks,^[2,8–10] laser ablation,^[11] and ink-jet printing.^[12,13] Although a small, monochrome, flat-panel display based on these materials has been demonstrated,^[14] each of these techniques has limitations that hinder the patterning of EL materials. For example, many of the processes associated with photolithography and lift-off—in particular, exposure to solvents—damage organic EL materials.^[6] As a result, complicated, multi-step processes^[15,16] are needed to create multi-colored arrays using this technique. The use of rigid, metal shadow masks,^[17] where an EL material is patterned on a surface by evaporation through the mask, is limited in resolution by the existence of an air gap between the mask and surface. This gap results in features of EL materials larger than the holes in the mask because of lateral diffusion and oblique patterning. The smallest features of an organic EL material that have been fabricated using a rigid, metal shadow mask had diameters of 80 μm .^[10] Furthermore, rigid masks cannot be used to pattern from the liquid phase or to pattern curved substrates. These limitations

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have meant that, in general, the quality of electroluminescence from patterns of small ($< 100 \mu\text{m}$) features of these materials has not been high: many techniques yield an uneven distribution of EL within a feature,^[7,11,18] or variations from pixel to pixel.^[6,12]

We have developed a straightforward, non-photolithographic method for patterning small ($\leq 50 \mu\text{m}$ diameter) features and have used it to pattern features of both *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1-1'-biphenyl-4,4'-diamine (TPD, a hole-transporting material) and tris(8-hydroxyquinoline) aluminum (Alq_3 , an emitter). When TPD forms a double layer structure with Alq_3 , between an indium tin oxide (ITO) anode and an aluminum cathode, application of a voltage to the device produces electroluminescence.^[19] A method for patterning TPD or Alq_3 at small size scales opens the possibility of creating arrays of EL features for use as pixels in high resolution optical displays. Our approach has been to fabricate elastomeric membranes that form a reversible, close seal when placed in

contact with a surface. These membranes serve as masks through which EL materials can be evaporated;^[20] when the membrane is peeled away, a pattern of EL material that matches the holes in the membrane remains on the surface. This procedure can be viewed as dry lift-off: no solvents are required to perform any of the steps involved in pattern transfer. By using two or more of these membranes in conjunction, we have also developed a simple way of patterning multiple colors of EL materials.

Figure 1 outlines the steps in the fabrication of elastomeric membranes. In this procedure, we spin-coated a thin layer of a pre-polymer of poly(dimethyl siloxane) (PDMS) onto a master that had been prepared by photolithography. The aspect ratios of the features on the master were usually less than or equal to unity. Spin-coating PDMS onto a master consisting of an array of parts created an elastomeric film containing an array of holes. The height of the features in photoresist set the maximum thickness of this membrane (3–100 μm thick). The rate and duration of spin-coating,

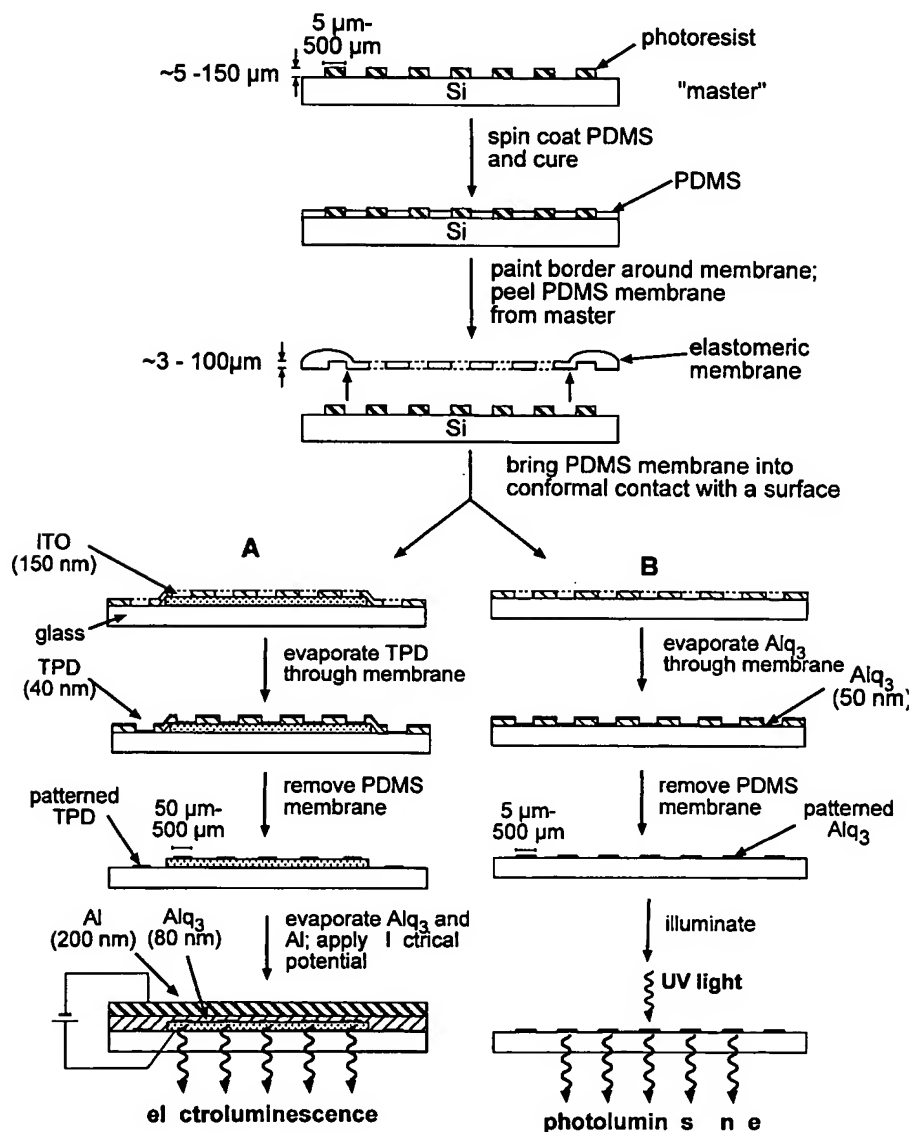


Fig. 1. Scheme for the fabrication of elastomeric membranes and their use as conformal shadow masks for patterning an EL material. A master, for example, an array of posts of photoresist on a silicon wafer, was created by photolithography. A pre-polymer of PDMS was then spin-coated onto the master so that the thickness of the layer of polymer was less than the height of the posts of photoresist. We cured the polymer at 65°C for 1 h. For the thinner membranes ($< 50 \mu\text{m}$ thick), we then painted and cured a thick border of PDMS around the features. Peeling the membrane away from the master yielded a flexible membrane of PDMS: the membrane contained an array of holes whose shape and pattern corresponded to those of the posts of photoresist. Membranes were fabricated with holes ranging in diameter from 5 to 500 μm ; the thicknesses of these membranes were 3–100 μm . A) Fabricating EL devices. We brought a PDMS membrane (30–100 μm thick) into conformal contact with a glass substrate coated in a 150 nm thick layer of ITO. After evaporating TPD (40 nm) through the membrane, we performed dry lift-off, i.e., we peeled off the membrane. We then deposited Alq_3 (80 nm) over the entire surface, followed by aluminum (2 nm wide strips) to form the device. An electrical potential was applied between the ITO anode and Al cathode, and electroluminescence was observed from the circular patterns of double layer structures of Alq_3 and TPD. B) PL from patterned Alq_3 . A PDMS membrane containing 5–500 μm diameter holes was brought into conformal contact with a silicon wafer. Alq_3 (50 nm) was evaporated through the membrane, and the membrane was peeled from the surface. The surface was then illuminated with UV light and PL was observed from the pattern of Alq_3 circles.

and the lateral dimensions and spacing of features on the master also determined the thickness,^[21] for example, spin-coating PDMS at 3000 rpm for 60 s onto 50 μm features, spaced by 50 μm , produced a membrane $\sim 45 \mu\text{m}$ thick, and spin-coating a 4:1 mixture of toluene/PDMS at 3000 rpm

for 40 s onto a wafer with 5 μm features spaced by 10 μm produced a membrane less than 3 μm thick. Figures 2A and 2B show scanning electron microscope (SEM) images of PDMS membranes containing holes with diameters of 50 μm and 5 μm , respectively. Spin-coating of the PDMS

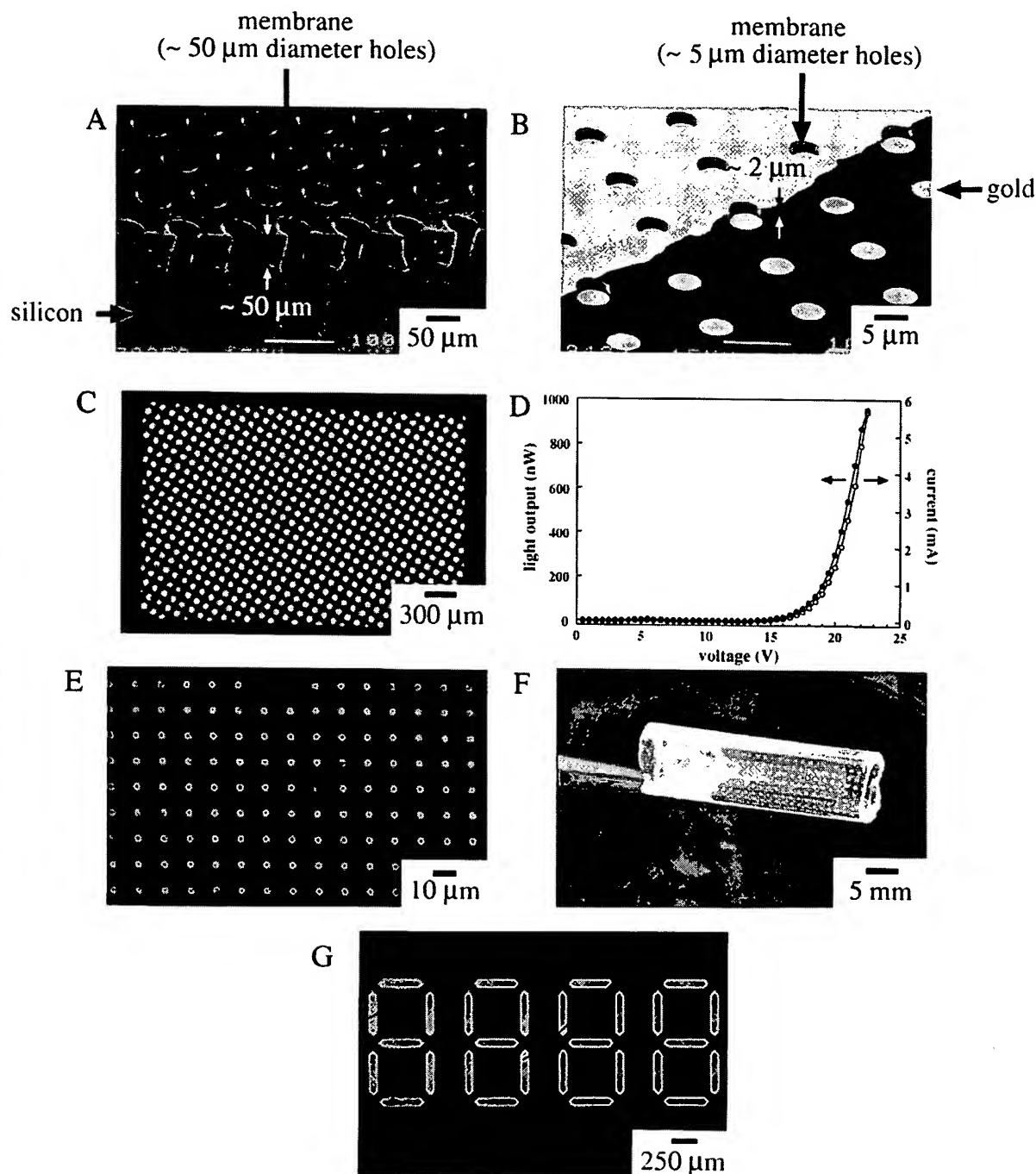


Fig. 2. A) SEM image of a PDMS membrane containing 50 μm diameter circular holes on a silicon wafer (the membrane is upside down). B) SEM image of a membrane containing 5 μm diameter circular holes sealed against a silicon wafer through which we had evaporated gold. One section of the membrane had been removed. C) EL device. An image of electroluminescence from 50 μm circles of double layer structures TPD and Alq₃ between an ITO anode and an Al cathode created using the procedure shown in Figure 1A. The average light output of the device was $\sim 160 \text{ Cd/m}^2$. D) I-V curve for device similar to the one shown in Figure 2C. E) PL. An image of PL from 3 μm circles of Alq₃ separated by 10 μm defined on a silicon wafer using the method shown in Figure 1B. F) Optical micrograph showing PL from Alq₃ patterned on a glass rod (outer diameter $\sim 6 \text{ mm}$) using an elastomeric membrane. G) PL from Alq₃ patterned with alphanumeric feature by dry lift-off. The master for this membrane was fabricated using rapid prototyping [27]—a technique in which a high-resolution transparency is used in place of a chrome mask to perform photolithography.

and release of the membrane did not destroy the master: we have spin-coated PDMS onto masters > 10 times to create multiple membranes without observable degradation in the features produced. We have not, however, established the ultimate durability of the masters.

The thickness of the elastomeric membrane determined both the area that could be patterned in a single run and the durability of the membrane. Membranes with thicknesses greater than or equal to $\sim 40\ \mu\text{m}$ (feature sizes > $50\ \mu\text{m}$) could be handled easily with tweezers, and would seal uniformly over large areas. Furthermore, when a membrane was placed in contact with a substrate, there was no elastic strain in the membrane and, therefore, no distortion of the holes. We have used membranes with these structural characteristics to pattern areas up to $20\ \text{cm}^2$ with reliable, undistorted transfer of patterns. These membranes were reusable: we usually rinsed the membranes with ethanol between uses. We have not determined the ultimate durability of these thicker membranes, but we have used a single membrane to pattern circles ($100\ \mu\text{m}$ diameter) of Alq_3 five times, and additional uses would have been possible. To facilitate the handling of membranes, particularly for the thinner membranes ($\leq 40\ \mu\text{m}$ thick), before removal from the master but after the membrane had cured, we painted and cured a thick ($\sim 2\ \text{mm}$) supporting border of PDMS around the edges of the membranes. For the thinnest ($\leq 5\ \mu\text{m}$ thick) membranes, which are required to pattern features with diameters $\leq 10\ \mu\text{m}$, the largest area that could be patterned in one step without distortion was $\sim 1\ \text{cm}^2$.^[22] These thin ($\leq 5\ \mu\text{m}$) membranes were also less durable than the thick membranes and would often tear during removal from the surface being patterned. As a result, we planned to use these membranes only once.

Figure 1 also illustrates the use of elastomeric membranes to fabricate EL devices by dry lift-off. We placed a PDMS membrane containing an array of circular holes ($50\ \mu\text{m}$ diameter, spaced by $50\ \mu\text{m}$) in conformal contact with a transparent, conducting ITO substrate, and evaporated a $40\ \text{nm}$ thick layer of TPD through the membrane. Performing the dry lift-off step, i.e., peeling the membrane away, left circles of TPD defined on the surface.^[23] Subsequent evaporation of a $80\ \text{nm}$ thick layer of Alq_3 (the emitting material) over the entire surface, followed by the evaporation of strips ($2\ \text{mm}$ wide) of aluminum produced an EL device. Applying an electrical potential of $\geq 14\ \text{V}$ between the ITO anode and aluminum cathode generated electroluminescence in the regions where double-layer structures had formed between the TPD and Alq_3 , i.e., in the patterned regions. Figures 2C and 2D show electroluminescence from a device composed of $50\ \mu\text{m}$ diameter circles and an I - V curve measured for a typical device, respectively.^[24] Light output from the device was as high as $160\ \text{Cd/m}^2$: this value represents an average from over the entire device. Light only originated from the double layer structure defined by the TPD: these circles only cover approximately one fifth of the area, so the actual brightness

of each emissive dot was five times this number. This brightness is more than sufficient for video applications.^[1] For optical devices containing discrete pixels, in addition to high intensity, it is important that the variation in light emission from dot-to-dot be small and, more importantly, that emission across a single dot be homogeneous. Other groups who have produced patterned organic devices have reported unevenness within EL features,^[7] variation from dot-to-dot,^[6,12] and emission only from the edges of features.^[18] The light distribution of individual EL dots created using dry lift-off was even (Fig. 2C); Figure 2C also shows that dot-to-dot variation in intensity was small.

An alternative way to produce EL devices based on these materials is to pattern features of Alq_3 on a continuous layer of hole-transporting material: we have used PDMS membranes to fabricate EL devices composed of arrays of double layer structures of 50 – $500\ \mu\text{m}$ diameter circles of Alq_3 on a different hole-transporting material, poly(*N*-vinylcarbazole) (PVK).^[25] To demonstrate the feasibility of using elastomeric membranes to create high resolution displays, we have also used the membranes to pattern features of Alq_3 with diameters of less than $10\ \mu\text{m}$. For example, Figure 2E shows photoluminescence (PL) from $5\ \mu\text{m}$ diameter circles of Alq_3 evaporated through a PDMS mask onto silicon. We have also used a similar approach to demonstrate that the flexibility of the PDMS membranes allows patterning on curved surfaces: we created a photoluminescent pattern of circles ($500\ \mu\text{m}$ diameter) of Alq_3 on glass tubing (diameter $\sim 6\ \text{mm}$) by sealing a membrane against the tubing and rotating it during the thermal evaporation of Alq_3 (Fig. 2F). We note that while these structures are photoluminescent, i.e., not electroluminescent, they illustrate the use of dry lift-off for patterning.

The patterns that can be created by these membranes are not limited to arrays of circles: for example, Figure 2G shows PL from an alphanumeric pattern of Alq_3 evaporated through a PDMS mask onto silicon. With a single membrane, however, there are constraints on the features that can be produced because the membrane must be continuous, self-supporting, and mechanically stable: features are limited to relatively simple, solid, discrete features. This limitation can be addressed by the use of two or three membranes, in sequential dry lift-off steps, that allow the fabrication of complex patterns.^[21]

We have also used two membranes to create multicolor, i.e., red, green, and blue (RGB), photoluminescent patterns of organic materials. Figure 3 illustrates schematically the simultaneous use of two membranes to create arrays of red, green, and blue circles by patterning mixtures of Alq_3 and dyes. The first membrane sealed against the substrate (in this case, silicon) and served to define every region on the substrate that would be patterned once all EL materials have been deposited—it can be thought of as a composite pattern. In this case, the membrane consisted of an array of $100\ \mu\text{m}$ diameter circular holes spaced by $100\ \mu\text{m}$. The second membrane was aligned above the first membrane and

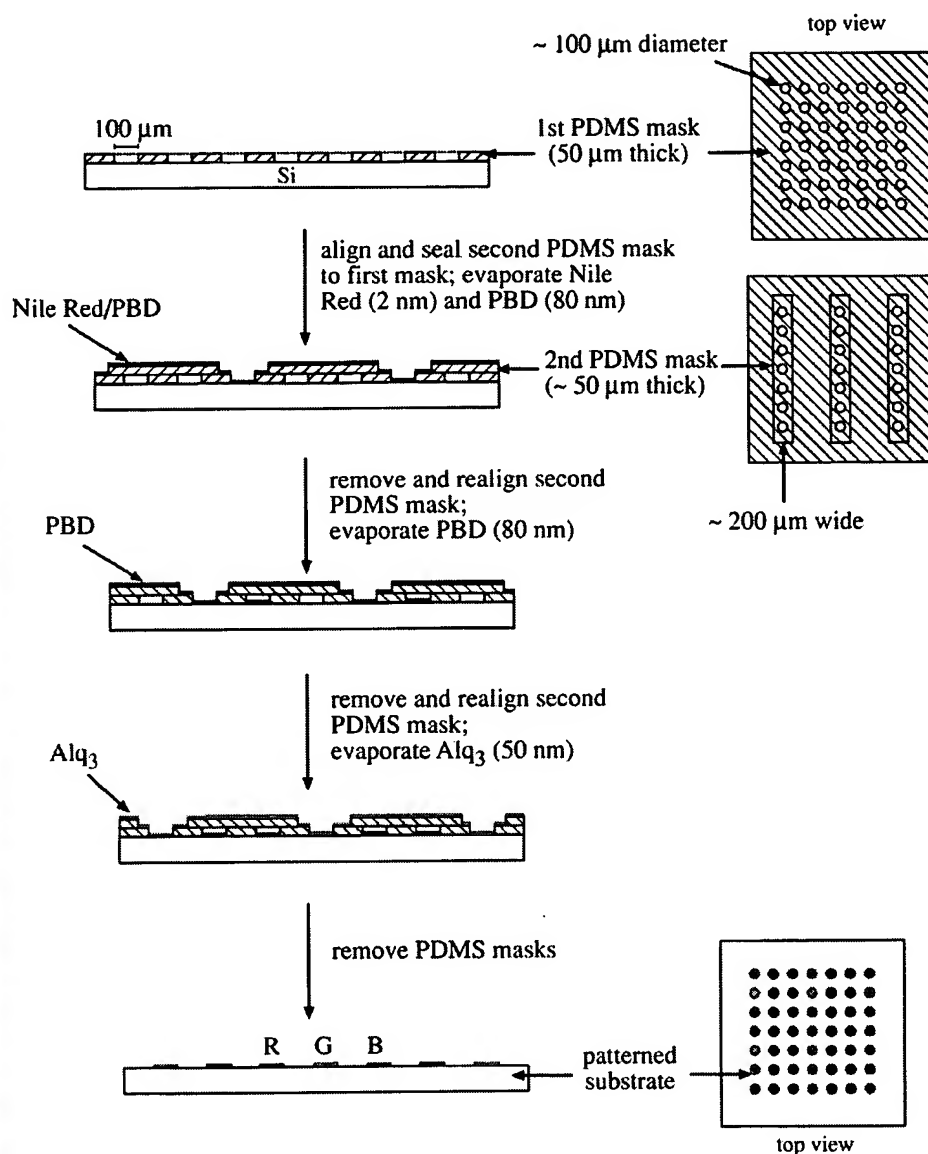


Fig. 3. Schematic illustration of the use of two elastomeric membranes to pattern multiple materials. A first elastomeric membrane, containing a pattern of open holes that defined the composite pattern (i.e., the pattern that is formed on the surface once all materials have been deposited), came into conformal contact with the substrate. In this case, the first membrane on the substrate consisted of an array of open, circular holes (100 μm diameter) spaced by 100 μm. Then a second membrane defined the regions to be patterned during a particular step. The second mask had open strips of 200 μm in width and ~1 cm in length that were spaced with a period of 600 μm—it was aligned to the first membrane so that every third row of circular holes was exposed. In a first deposition, we deposited Nile Red (2 nm) followed by a 10:1 mixture PBD:Coumarin 47 (80 nm) to form red dots. We removed and realigned the second membrane so that the adjacent rows of holes became exposed. We evaporated PBD:Coumarin 47 (80 nm) to form blue dots, and then repeated the alignment step and evaporated Alq₃ (50 nm) to form green dots.

defined the region of the composite pattern of EL material that would be patterned during a particular step. The second membrane had 200 μm wide, ~1 cm long, open strips that were spaced with a period of 600 μm. Every third row of circular holes in the first membrane was exposed at any given time. Once one EL material had been deposited onto the substrate, the second membrane was removed, shifted and replaced, or replaced by a different membrane, before a second EL material was deposited. In this case, the second membrane was the same each time. Multiple patterning steps in this way create a composite pattern composed of several different EL materials. Although patterns of multiple colors could, in principle, be created using one mask and repositioning it after every deposition, the use of more than one mask has two main advantages. First, the composite pattern defined by the first mask means that the second mask can have openings with diameters larger than the features being patterned: this property makes alignment during repositioning easier than if a single mask was

used. Second, the use of a second mask reduces the chance of damaging material patterned on the substrate during repositioning of the mask. Figure 4 shows a large area (1 cm²) and detail of PL from patterned dots of three different colored materials patterned using two elastomeric membranes. We aligned the masks by hand under a stereomicroscope: alignment by this procedure at the 100 μm level was simple. This level of registration meets the minimum requirement for high-resolution RGB displays, and RGB displays with smaller features could certainly be produced in this way. At smaller scales for production, however, we would need to use an alignment jig, i.e., to mount the substrate and masks on supports that could be positioned relative to one another.

Our data show that the use of PDMS membranes is a plausible method for patterning EL materials, and can be used to produce functional electroluminescent devices with high quality features as small as 50 μm. Using PDMS membranes and a dry lift-off procedure to pattern EL materials

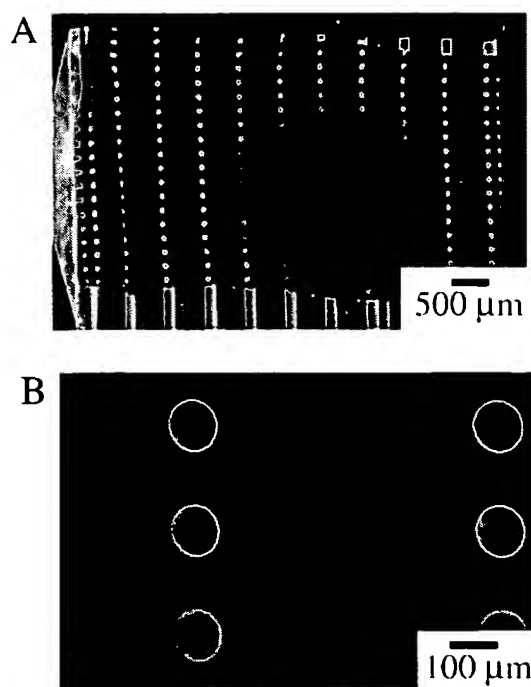


Fig. 4. Optical micrograph of PL from 100 μm diameter circular features formed by use of two elastomeric membranes. A) PL from a large area (1 cm^2) of three-color dots. The red dots are formed from Nile Red and PBD:Coumarin 47, the blue dots from PBD:Coumarin 47, and the green dots from Alq₃. B) PL from magnified area of the large array shown in A).

has several advantages over the techniques that have received most attention previously: photolithography/conventional lift-off, and rigid shadow masks. First, the fabrication of these membranes is simpler than machining of metals^[26] that is normally used to fabricate metal masks, or photolithography to form patterns in photoresist. The membranes (> 10 μm thick) are also reusable: they are not destroyed by the patterning step as photoresist is. They are inexpensive enough that they can be discarded after only one or two uses. Second, since these membranes conform to and seal against the substrate being patterned and can be removed with a pair of tweezers, they are compatible with a wide range of materials and processes that are not restricted to those presented here.^[21] In particular, the membranes can be used to pattern EL materials degraded by exposure to solvents and UV light, and potentially allows them to be used to pattern from the liquid phase. The sealing of the membrane to the substrate also maximizes the resolution that can be obtained from a shadow mask. Third, the PDMS membranes are softer than metal masks and are, therefore, less likely to damage by abrasion either the material being patterned or the substrate: the quality of electroluminescence from features patterned using these membranes indicated that the EL organic materials were not damaged by removal of the mask, and SEM images of patterns of another, albeit harder, material, gold, did not reveal any damage at the sub-micrometer level.^[21] Fourth, the flexibility of the PDMS membranes allows them to conform to and pattern curved surfaces that would otherwise be difficult to pattern even with a thin, flexible metal mask

that would have to be clamped in place during patterning. Fifth, using two or more membranes simplifies the fabrication of patterns of multiple colors: schemes for patterning multiple colors using conventional methods require encapsulation of already deposited materials and often cause degradation of the devices.^[15,16] We also note that the minimum size of the features we have created using these membranes (5 μm) is smaller than the minimum reported using rigid metal shadow masks (80 μm).^[10]

These membranes do, however, have limitations. Only simple, solid, discrete patterns can be produced using a single membrane. For optical displays, which typically require only circular features, this limitation does not present a significant problem. For situations where it is an issue, we have used multiple membranes in sequential, registered dry lift-off steps to create complex patterns.^[21] Distortion of the membranes could also result in less reliable transfer of patterns to surface. We did not experience problems with distortion of membranes thicker than 30 μm ; for thinner membranes, deformations meant that only small areas of membrane (< 1 cm^2), supported by the thicker surrounding layer of PDMS, could be used to pattern. We have fabricated membranes composed of layers of PDMS and epoxy: these two-layer membranes are more rigid than membranes fabricated only from PDMS and are less prone to distortion.^[21] In some cases, intentional distortion of the membrane could be used to produce new features.

In summary, we believe these membranes are well suited for patterning any electroluminescent dye deposited by evaporation and will be most useful in the fabrication of EL devices with features with diameters ranging from 10–100 μm . They also allow devices to be fabricated on non-planar substrates. We believe that the conformal nature of the mask will make it possible to pattern EL materials by methods other than evaporation, e.g., using CVD and liquid phase deposition.^[21] By designing a configuration of electrodes that is addressable, and by using an appropriate set of elastomeric membranes, we anticipate that it should also be possible to use this method to create a fully functional EL RGB display with feature sizes less than 50 μm .

Experimental

Fabrication of Masters: The master consisted of an array of features in photoresist created on a silicon wafer. It was generated either by rapid prototyping (for feature sizes > 50 μm) [27]—a method that uses a high-resolution transparency as the photomask for photolithography—or by performing standard photolithography with a chrome mask (for feature sizes < 50 μm). For feature sizes greater than 50 μm (less than 50 μm), we used SU-850 (SU-85) resist (Microlithography Chemical Corporation, Newton, MA). Spin-coating the resist at 5000 rpm for 20 s (6000 rpm for 40 s), produced a film approximately 50 μm thick (5 μm thick). After baking the resist at 105 °C for 5 min (5 min), we exposed it to UV light (λ_{max} = 365 nm, 406 nm, 436 nm) for 1 min (5 s) through a mask using a Karl Suss Mask Aligner. We developed the features in propylene glycol methyl ether acetate (PGMEA) for ~5 min (1 min) after the wafer had been baked for 15 min (5 min) at 105 °C. Subsequent surface treatment of the silicon wafer by exposure to the vapor of perfluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (United Chemical Technology, Bristol, PA) in a vacuum desiccator prevented adhesion of the elastomer to the wafer during the next step.

Fabrication of Elastomeric Membranes: We fabricated elastomeric membranes by spin-coating a liquid pre-polymer of PDMS (Sylgard 184; Dow Corning, Midland, MI) onto a master. The rate of spinning was set so that the thickness of the layer of PDMS was less than the height of the posts of photoresist: for example, for posts 50 μm high, we spin-coated PDMS at 3000 rpm for 60 s to produce an approximately 45 μm thick film; for posts 5 μm high, we spin-coated a 1:4 mixture of PDMS/toluene at 3000 rpm for 40 s to yield a film less than 3 μm thick. After curing the PDMS, a thicker (~2 mm) layer of the liquid pre-polymer was painted around the outside of the pattern and cured: this layer made it easier to peel the elastomer from the master.

Fabrication of EL Devices: ITO-coated glass slides were cleaned by sonicating them in a 3:1 mixture of deionized water and detergent (Lysol Deodorizing Cleaner, Reckitt and Colman, Inc., Montvale, NJ) for 15 min, then in water for 30 min, in ethanol for 15 min, and were finally blown dry in a stream of N_2 . We placed a PDMS membrane against the ITO-coated slide using a pair of tweezers and the membrane sealed conformally against the substrate. For the TPD/Alq₃ EL device, 40 nm of TPD (courtesy Dr. Martin Abkowitz, Xerox Corporation, Rochester, NY) was thermally evaporated (~0.2–0.3 nm/s; base pressure $\sim 5 \times 10^{-6}$ torr) onto the membrane containing 50 μm holes, and the membrane was then peeled away from the substrate using a pair of tweezers. We thermally evaporated 80 nm of Alq₃ (Aldrich, Milwaukee, WI; purified by sublimation) over the entire array of TPD dots at a rate of 0.2–0.3 nm/s (base pressure $\sim 5 \times 10^{-6}$ torr), followed by 2 mm wide strips of aluminum (~20 nm; ~1 nm/s). To observe electroluminescence from the array of 50 μm diameter double layer structures, an electric potential (≥ 14 V) was applied between the ITO anode and the aluminum cathode.

Fabrication of Photoluminescent Structures: Alq₃ was patterned by thermal evaporation (~0.5 nm/s; base pressure $\sim 5 \times 10^{-6}$ torr) through the membrane sealed against either silicon or glass. After peeling away the PDMS membrane, we observed PL from the patterns of Alq₃ under UV light.

Fabrication of Multicolor Patterns of EL Materials: We sealed a membrane containing an array of open, circular holes (100 μm diameter, spaced by 100 μm) against a silicon wafer. A second membrane containing open strips of 200 μm in width and ~1 cm in length that were spaced with a period of 600 μm was aligned to the first membrane so that every third row of circular holes was exposed. In a first deposition, we evaporated Nile Red (2 nm at ~0.1 nm/s; Aldrich, Milwaukee, WI) followed by a 10:1 mixture of 2-(4-biphenyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole (PBD; Aldrich, Milwaukee, WI):Coumarin 47 (Lambda Physik, Ft. Lauderdale, FL) (80 nm at ~1.5 nm/s) to form red dots and then realigned the second membrane so that the adjacent rows of pores became exposed. We evaporated PBD: Coumarin 47 (80 nm; rate ~1.5 nm/s) to form blue dots, and then repeated the alignment step and evaporated Alq₃ (50 nm at ~0.3 nm/s) to form green dots.

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Colloidally Prepared HgTe Nanocrystals with Strong Room-Temperature Infrared Luminescence**

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Nanometer-sized semiconductor particles (often referred to as nanoclusters, nanocrystals, or quantum dots) belong to a state of matter lying in the transition region between molecules and bulk materials. Because of the quantum confinement effect, nanocrystals show unique physical and chemical properties when they are smaller than the dimension of the exciton.^[1–3] Due to the large surface-to-volume ratio, in small particles the surface chemistry of the nanocrystals plays yet another important role. Control of the

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